Theoretical models for fluid thermodynamics based on the quasi-Gaussian entropy theory

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Chapter 7

Towards an equation of state for sub- and supercritical water based on the quasi-Gaussian entropy theory

In this article we applied the confined Gamma statistical state of the quasi-Gaussian entropy theory to describe the thermodynamic functions of water along isochores within the temperature range 273-1073 K and density range 0-60 mol/dm^3. Different methods to obtain the necessary parameters of the model along the isochores were evaluated and their accuracy compared, in order to find an efficient way of parametrizing an overall equation of state using only a limited set of experimental data, preferably at low temperature. The confined Gamma state level of the theory is able to describe very well the thermodynamics of water including also the critical point region of the phase diagram.

7.1 Introduction

Despite the tremendous developments in statistical mechanics during the last century, the construction of general fluid equations of state (EOS), applicable to both polar and apolar molecules and based on a strong theroretical background, is still a challenging problem. The crucial point is the evaluation of the configurational partition function, which is a high-dimensional integral over all particle coordinates. For any reasonably realistic Hamiltonian this integral cannot be calculated exactly, and often severe approximations have to be made.

Starting with van der Waals (1873), a number of empirical (cubic) equations of state have therefore been developed, such as the Soave-Redlich-Kwong[35,36] and Peng-Robinson[37] EOS, which are mainly used for apolar molecules like alkanes.[34]

More based on statistical mechanics are among others the statistical associating fluid theory (SAFT),[104–108] perturbed hard and soft chain theories[109–118] and EOS based on integral equations.[3]

In a recent article[119] we derived an equation of state for the Lennard-Jones (LJ) fluid, using the quasi-Gaussian entropy (QGE) theory as a basis. In the QGE theory,[11,12,49] the excess free energy with respect to a properly chosen reference state, usually statistical mechanically expressed in terms of the high-dimensional configurational partition function, is rephrased in terms of a one-dimensional expectation value over the probability distribution of the "potential" energy of the system. In this way the dimensionality of the problem is strongly reduced, and only assumptions on the specific model energy distributions are required. Each type of (model) distribution yields a unique set of thermodynamic functions, the "statistical state" of the system.

In this article we will focus on the thermodynamic description of water. In previous articles we already explored its thermodynamics for some specific gas and liquid isochores,[12,13,49] finding that the confined Gamma state within the QGE theory is able to describe the behaviour of water along those isochores with high accuracy. Since our aim is to construct an EOS roughly within the same temperature range as these previous investigations, we decided to use this confined Gamma state isochore description as the basis of the equation of state. Note that for the recent Lennard-Jones EOS we used a slightly more complex isochore model, including a simple perturbation term.[119] However, since the temperature range which is covered by the LJ EOS ($0.6 \leqslant T/T_c \leqslant 15.0$) is much larger than for water ($0.4 \leqslant T/T_c \leqslant 1.7$, with T_c the critical temperature), the perturbation term is therefore likely to be negligible in this case, and we decided to use the simpler confined Gamma state.

In this article we will specifically address (1) the critical point region and show that even there the confined Gamma state level of the theory gives an excellent description and (2) investigate what is the minimal amount of experimental information needed to obtain the parameters of the model along the isochores.

The parameters may then be modelled along a reference isotherm T_0 using

a nummerical interpolation scheme or analytical interpolation functions, as was done for the LJ equation of state.[119]

7.2 Temperature dependence

The QGE theory, in its original formulation in the canonical ensemble,[11,12,49] rephrases the thermodynamic excess functions (like the excess free energy, entropy, energy, pressure etc.) with respect to a properly chosen reference condition in terms of the properties of the probability distribution function $\rho(\mathcal{U}')$ of the overall instantaneous "potential" energy $\mathcal{U}'$ of the system. This distribution is for macroscopic systems close to a Gaussian ("quasi-Gaussian"). Each type of (model) distribution function defines in a unique way via its moment generating function[20,21,60] the complete set of thermodynamic functions, i.e., the "statistical state" of the system.

The confined Gamma state, with which the water EOS can be constructed, is in fact based on two assumptions. (1) A part of configurational space of the ideal gas may be inaccessible for water at real conditions due to hard-body excluded volume effects (the phase-space confinement), and (2) the probability distribution function $\rho(\mathcal{U}')$ within the accessible part of configurational space is given by a Gamma distribution.[20,120] From this the thermodynamic functions follow in an exact way. Using a general approximation for the treatment of the vibrational partition function,[12,49] and the fact that water has no semi-classical internal degrees of freedom, the "potential" energy $\mathcal{U}'$ is simply equal to the energy of the actual system minus that of the ideal gas at the same temperature and density.

The excess Helmholtz free energy with respect to the ideal gas at the same temperature and density (the ideal reduced free energy A') can now be written as the sum of two terms; the first one is linked to the accessible part of configurational space (the confined ideal reduced free energy A^*, modelled via the properties of the Gamma distribution), and the second one is a purely entropic term due to the confinement (A_{conf}):

$$A'(T) = A(T) - A_{id}(T) \qquad = A^*(T) + A_{conf}(T) \tag{7.1}$$

Similarly, we have for the excess entropy, energy, isochoric heat capacity, pressure and its first two temperature derivatives

$$S'(T) = S(T) - S_{id}(T) \qquad = S^*(T) + S_{conf}(T) \tag{7.2}$$

$$U'(T) = U(T) - U_{id}(T) \qquad = U^*(T) \tag{7.3}$$

$$C'_V(T) = C_V(T) - C_{V\,id}(T) \quad = C^*_V(T) \tag{7.4}$$

$$p'(T) = p(T) - p_{id}(T) \qquad = p^*(T) + p_{conf}(T) \tag{7.5}$$

$$\frac{\partial p'(T)}{\partial T} = \frac{\partial p(T)}{\partial T} - \frac{\partial p_{id}(T)}{\partial T} \quad = \frac{\partial p^*(T)}{\partial T} + \frac{\partial p_{conf}(T)}{\partial T} \tag{7.6}$$

$$\frac{\partial^2 p'(T)}{\partial T^2} = \frac{\partial^2 p(T)}{\partial T^2} - \frac{\partial^2 p_{id}(T)}{\partial T^2} = \frac{\partial^2 p^*(T)}{\partial T^2} \tag{7.7}$$

where

$$A_{conf}(T) = -kT \ln \epsilon \tag{7.8}$$

$$S_{conf}(T) = k \ln \epsilon \tag{7.9}$$

$$p_{conf}(T) = \xi T \tag{7.10}$$

$$\frac{\partial p_{conf}(T)}{\partial T} = \xi \tag{7.11}$$

with ϵ the (temperature independent) fraction of configurational space that is accessible to the molecules,[12,49] and $\xi = k(d \ln \epsilon / dV)$. Furthermore, within the Gamma state the confined ideal reduced properties as a function of the temperature are given by[12,49]

$$A^*(T) = U_0^* - \frac{T_0 C_{V0}^*}{\delta_0} - \frac{T C_{V0}^*}{\delta_0^2} \ln \{1 - \delta(T)\} \tag{7.12}$$

$$U^*(T) = U_0^* + (T - T_0)\, C_{V0}^* \, \frac{\delta(T)}{\delta_0} \tag{7.13}$$

$$S^*(T) = \frac{C_{V0}^*}{\delta_0^2} \left[\delta(T) + \ln \{1 - \delta(T)\} \right] \tag{7.14}$$

$$C_V^*(T) = C_{V0}^* \left(\frac{\delta(T)}{\delta_0} \right)^2 \tag{7.15}$$

$$p^*(T) = p_0^* + B_0^* + B_1^* \frac{1 - \delta(T)}{1 - \delta_0} + B_2^* \left(\frac{T}{T_0} \right) \ln \{1 - \delta(T)\} \tag{7.16}$$

$$\frac{\partial p^*(T)}{\partial T} = \frac{B_1^*}{T_0} \frac{\delta^2(T)}{\delta_0} + \frac{B_2^*}{T_0} \left[\delta(T) + \ln \{1 - \delta(T)\} \right] \tag{7.17}$$

$$\frac{\partial^2 p^*(T)}{\partial T^2} = -2 \frac{B_1^*}{T_0^2} \frac{(1 - \delta_0)}{\delta_0^2} \delta^3(T) + \frac{B_2^*}{T_0^2} \left(\frac{T_0}{T} \right) \delta^2(T) \tag{7.18}$$

with

$$\delta(T) = \frac{M_3(T)}{2kT M_2(T)} = \frac{T_0 \delta_0}{T(1 - \delta_0) + T_0 \delta_0} \tag{7.19}$$

In these expressions T_0 is an arbitrary reference temperature, and a zero subscript denotes that the property is evaluated at T_0. The coefficients B_i^*, which are a function of T_0, δ_0, $\partial p_0^*/\partial T$ and $\partial^2 p_0^*/\partial T^2$, are given by[12,49]

$$B_i^* = A_{i1} T_0 \left(\frac{\partial p_0^*}{\partial T} \right)_V + A_{i2} T_0^2 \left(\frac{\partial^2 p_0^*}{\partial T^2} \right)_V \qquad i = 0, 1, 2 \tag{7.20}$$

with

$$A_{01} = -\frac{2(1-\delta_0)\ln(1-\delta_0)+\delta_0}{D} \qquad A_{02} = \frac{1}{\delta_0}\frac{(1-\delta_0)\ln(1-\delta_0)+\delta_0}{D}$$
$$A_{11} = \frac{\delta_0}{D} \qquad A_{12} = -\frac{1}{\delta_0}\frac{\ln(1-\delta_0)+\delta_0}{D} \tag{7.21}$$
$$A_{21} = \frac{2(1-\delta_0)}{D} \qquad A_{22} = \frac{1}{D}$$

and

$$D = 2(1-\delta_0)\ln(1-\delta_0) + \delta_0(2-\delta_0) \tag{7.22}$$

The function $\delta(T)$, Eq. 7.19, which is proportional to the ratio of the third and second central energy moments M_3 and M_2, is linked to the skewness of the energy distribution: for $\delta < 0$ the distribution is asymmetric to the left, yielding a negative Gamma state, and for $0 < \delta < 1$ the distribution is asymmetric to the right, providing a positive Gamma state. As discussed elsewhere,[12,13,49] only the positive Gamma state is completely physically acceptable. The negative Gamma state must be regarded as a (good) approximation to a more complex statistical state.

Note that the free energy and its temperature derivatives along an isochore are completely specified by U_0^*, C_{V0}^*, δ_0 and ϵ. For the density derivatives of A' like the pressure, also p_0^*, $\partial p_0^*/\partial T$, $\partial^2 p_0^*/\partial T^2$ and ξ are required. These latter four parameters are via usual thermodynamic expressions related to the density derivatives of the first four properties.

7.3 Density dependence

For the water EOS we could describe the density part in the same way as was done previously for the Lennard-Jones equation of state based on the perturbed confined Gamma state description along the isochores,[119] i.e., via the explicit density dependence of the four parameters U_0^*, C_{V0}^*, δ_0 and ϵ for the free energy, and of the other four parameters p_0^*, $\partial p_0^*/\partial T$, $\partial^2 p_0^*/\partial T^2$ and ξ for the pressure, along a reference isotherm T_0. In fact, other interpolation procedures could be used (along any reference line in the ρ_N,T diagram, not necessarily an isotherm), and even the combination of the general isochore model used in this paper with another QGE statistical state, valid for a single ρ_N,T reference line (e.g. based on the enthalpy fluctuations along an isobar[70]).

In this article, however, we will only focus on the isochore description, and not on the interpolation scheme, as the use of different interpolation procedures is mainly a "technical problem" which will be addressed elsewhere, once the isochore model is fully defined.

As usual,[12,49,86,119] the confinement in configurational space is described by a hard-sphere model, based on the Carnahan-Starling EOS:[33]

$$k \ln \epsilon = Nk \, \frac{(3\eta^2 - 4\eta)}{(1-\eta)^2} \tag{7.23}$$

$$\xi = k \frac{d \ln \epsilon}{dV} = -\rho_N k \, \frac{(2\eta^2 - 4\eta)}{(1-\eta)^3} \tag{7.24}$$

where $\rho_N = N/V$ is the number density, $\eta = \rho_N v$ is the packing fraction with $v = \pi\sigma_{HS}^3/6$ the hard sphere volume per molecule and σ_{HS} the corresponding hard-sphere diameter. This in fact reduces the two parameters ϵ and ξ per isochore to a single overall coefficient v (or σ_{HS}).

7.4 Experimental data and parametrization procedure

Experimental data of p, H and S were taken from the steam tables of Schmidt[39] for $p \leqslant 1000$ bar, and from Burnham *et al.*[46] for $1000 \leqslant p \leqslant 10\,000$ bar. Ideal gas values of H and S were taken from the tables of Frenkel *et al.*,[48] and fitted to polynomials in the temperature range $200 < T < 1300$ K, see Table 7.1. As is common practice in steam tables, in Refs. 39 and 46 the values of the liquid enthalpy and entropy at the triple point are set to zero, in contrast to the absolute ideal gas values of Frenkel *et al.* The difference in the ideal gas values at the triple point due to this change of zero point was estimated to be 122.685 J/mol K for the entropy and 45.0622 kJ/mol for the enthalpy. From this the ideal reduced thermodynamic properties were calculated at 14 isochores, at densities $\rho_N = 0.5$, 1.0, 5.0, 10.0, 15.0, $\cdots$, 60.0 mol/dm^3. Errors were estimated using standard propagation of errors formulas and the uncertainties given by the different authors, i.e., 0.1% in V, S and H for values of Schmidt and Frenkel *et al.*, and 0.3% in V and S and 0.6% in H for values of Burnham *et al.*

Since the EOS is highly non-linear in the parameter δ_0, an overall fit at once was impossible. We therefore used the following procedure.

(1) The reference isotherm T_0 was chosen to be 673 K, which is about 25 K above the critical temperature T_c.

(2) The value $v = 0.00620489$ dm^3/mol (or $\sigma_{HS} = 2.6998$ Å) was adopted from Ref. 49, since (a) it was based already on a reasonable amount of data, using the same isochore model, and (b) since the value of σ_{HS} was in good agreement with values obtained by various other models.[12,49] Via Eqs. 7.23 and 7.24 for each density the values of ϵ and ξ are therefore also known.

(3A) For all 14 isochores the experimental confined ideal reduced free energy $A^* = A' + kT \ln \epsilon$ was fitted by the following expression, a combination of Eq. 7.12

i	h_i	s_i
0	-0.0545743241	-9.11903093
1	3.23771795e-4	0.0336803983
2	-6.64314517e-7	-2.60034146e-6
3	9.95080676e-10	4.8544961e-9
4	-9.66207188e-13	4.12113426e-12
5	5.80422330e-16	-6.90510548e-15
6	-1.95730111e-19	3.40742863e-18
7	2.82854763e-23	-5.91360001e-22

Table 7.1: Coefficients for the polynomial fits of the ideal gas values of Frenkel et al., *Ref. 48. Using the zero point values of H and S as in Schmidt and Burnham* et al. *(Refs. 39 and 46), the ideal gas values within the temperature range* $200 < T < 1300$ *K are* $H_{id} = 45.0622 + \sum_{i=0}^{7} h_i T^i$ *(kJ/mol) and* $S_{id} = 0.122685 + \sum_{i=0}^{7} s_i T^i$ *(kJ/mol K), with* T *in K.*

and Eq. 7.14, yielding $\delta_{0,loc}$:

$$A^*(T;\delta_{0,loc}) = U^*_{0,loc,exp} - S^*_{0,loc,exp}\left[\frac{T_{0,loc}\delta_{0,loc} + T\ln\left\{\dfrac{T(1-\delta_{0,loc})}{T(1-\delta_{0,loc})+T_{0,loc}\delta_{0,loc}}\right\}}{\delta_{0,loc}+\ln(1-\delta_{0,loc})}\right] \tag{7.25}$$

where for each isochore a different "local" reference temperature $T_{0,loc}$ was used, approximately 20 to 30 K above the coexistence line, and $U^*_{0,loc,exp}$ and $S^*_{0,loc,exp}$ are the corresponding experimental values of U^* and $S^* = S'_{exp} - k\ln\epsilon$. We decided to use a local, low-temperature $T_{0,loc}$ at each isochore, since (a) experiments to obtain experimental values at relatively low temperature are more feasable than at for example the common reference isotherm $T_0 = 673$ K, especially at high density, and (b) the values are likely to be more reliable.

(3B) Alternatively, to assess the best way to obtain the parameters with the least data as possible, we also estimated $\delta_{0,loc}$ at each isochore from the experimental energy and entropy data at $T_{0,loc}$ and only one extra experimental value of U^* at a somewhat higher temperature $T = T_{0,loc} + 20$, 40 or 60 K, by numerically solving $\delta_{0,loc}$ from

$$U^*(T;\delta_{0,loc}) = U^*_{0,loc,exp} + S^*_{0,loc,exp}\frac{\delta^2_{0,loc}}{\delta_{0,loc}+\ln(1-\delta_{0,loc})} \times \frac{T_{0,loc}(T-T_{0,loc})}{T(1-\delta_{0,loc})+T_{0,loc}\delta_{0,loc}} = U^*_{exp}(T) \tag{7.26}$$

i.e., a combination of Eqs. 7.13 and 7.14.

(4) The values of U_0^*, S_0^* and δ_0 at the common reference isotherm $T_0 = 673$ K were calculated from the "local" $T_{0,loc}$ values, using Eqs. 7.13, 7.14 and 7.19, where $C_{V0,loc}^* = S_{0,loc}^* / \left[1/\delta_{0,loc} + \ln(1-\delta_{0,loc})/\delta_{0,loc}^2\right]$.

(5A) Per isochore, the input properties of the pressure equation (Eq. 7.16), i.e., p_0^*, $\partial p_0^*/\partial T$ and $\partial^2 p_0^*/\partial T^2$, were obtained by a least-square fit on the experimental pressure data, using the value of δ_0 obtained from step **(3A)**.

(5B) Alternatively, the "local" pressure parameters $p_{0,loc}^*$, $\partial p_{0,loc}^*/\partial T$ and $\partial^2 p_{0,loc}^*/\partial T^2$ were obtained from a local second order polynomial fit on experimental pressure data in a temperature window of about 100-120 K around $T_{0,loc}$, using the three different values of $\delta_{0,loc}$ as obtained from step **(3B)**, giving three sets of "local" pressure parameters.

(6) The values of p_0^*, $\partial p_0^*/\partial T$ and $\partial^2 p_0^*/\partial T^2$ at the common reference isotherm $T_0 = 673$ K were calculated from the "local" $T_{0,loc}$ values of step **(5B)**, using Eqs. 7.16, 7.17 and 7.18.

In total we thus obtained four different sets of parameters: one set via fitting of A^* and p (steps **(3A)** and **(5A)**: set **1**), the other sets via single-point evaluations of U^* at 20, 40 or 60 K above $T_{0,loc}$ (step **(3B)**), each combined with a local evaluation of the pressure parameters (step **(5B)**): sets **2**, **3** and **4**.

7.5 Results and comparison

In Figs. 7.1 and 7.2 we show experimental values of the excess energy U^* and the pressure p, together with the Gamma state predictions using parameter sets **1** (based on fits on A^* and p') and **4** (single point energy evaluation at $T_{0,loc}+60$ K, local pressure evaluation). The curves of sets **2** and **3** are very similar to those of set **4**. In previous papers (Refs. 13 and especially 49) we have already presented isochore data at typical gas and liquid densities, but never in the vicinity of the critical point. We here therefore show data at $\rho_N = 10$, 15, 20 and 25 mol/dm^3, where the critical density of water is $\rho_{Nc} = 17.51$ mol/dm^3 (Ref. 39). The figures demonstrate that both Gamma states are in very good agreement with the experimental data. Even the curves based on very little information (set **4**) are for U^* always within the experimental errors, and it is clear that there are no special difficulties in applying this form of the QGE theory in the canonical ensemble (using the ideal reduced energy distribution) close to the critical point.

The behaviour of the parameters U_0^*, C_{V0}^* and δ_0 for set **1** as a function of density at the reference isotherm $T_0 = 673$ K is shown in Fig. 7.3. The behaviour of the parameters of sets **2**-**4** is almost identical.

Clearly, at $\rho_N \sim 5$ mol/dm^3 the distribution is the most asymmetric to the left ($\delta_0 < 0$, negative Gamma state), and with increasing density the repulsive interactions are enhanced, which contribute to right-hand tail of the distribution. At $\rho_N \sim 37$ mol/dm^3 the distribution is almost symmetrical (Gaussian state with

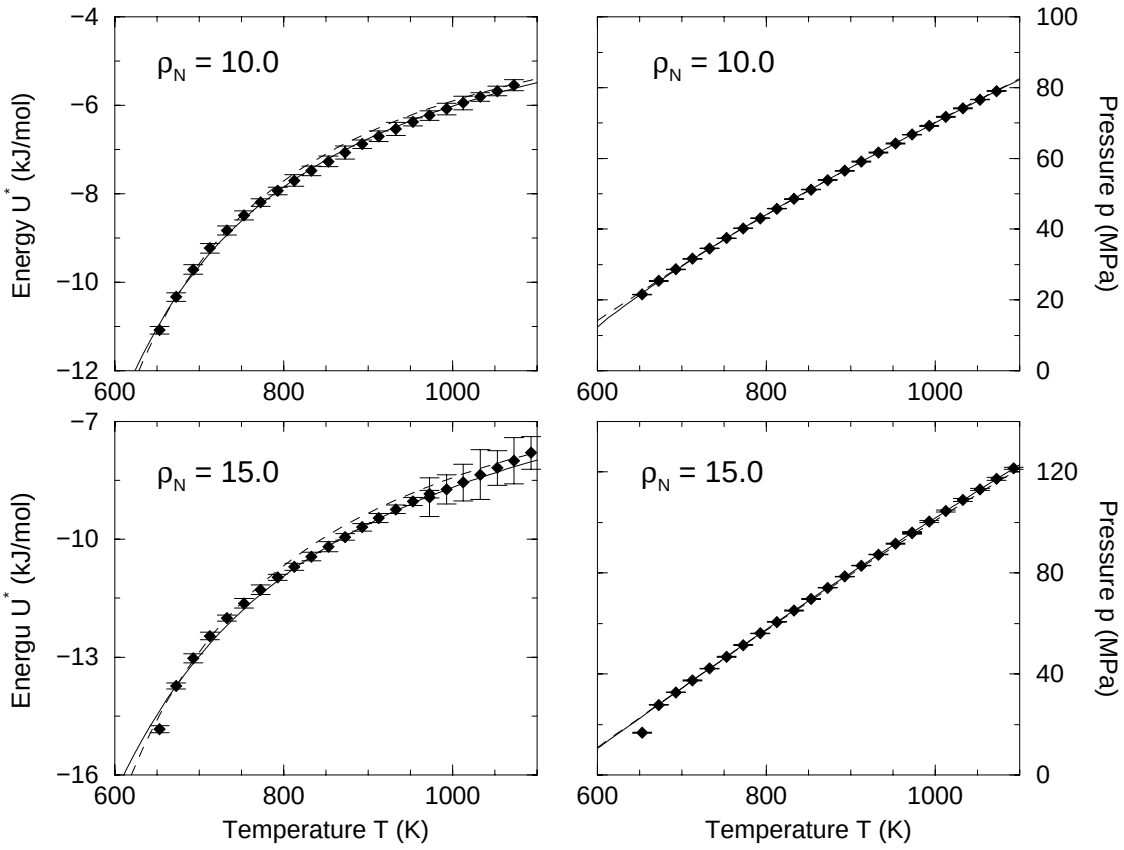

Figure 7.1: Experimental data of U^* and p for $\rho_N = 10$ and 15 mol/dm^3 (♦), and Gamma state predictions: parameter set **1** *(——) and set* **4** *(– – –).*

$\delta_0 = 0$), in accordance with previous findings,[49] and increasing the density even more, the distribution is asymmmetric to the right ($\delta_0 > 0$, yielding a positive Gamma state).

To have an overall measure of the accuracy of the different methods to obtain the parameters of the Gamma states at each isochore, for the four sets of parameters we calculated several statistics. For a property X (A', U^* and p) we evaluated the value of χ^2, defined as

$$\chi^2 = \sum_i^{N_{data}} \left(\frac{X_i - X_{i,exp}}{\sigma_{X_{i,exp}}} \right)^2 \tag{7.27}$$

where $\sigma_{X_{i,exp}}$ is the experimental error in $X_{i,exp}$, the root mean square deviation

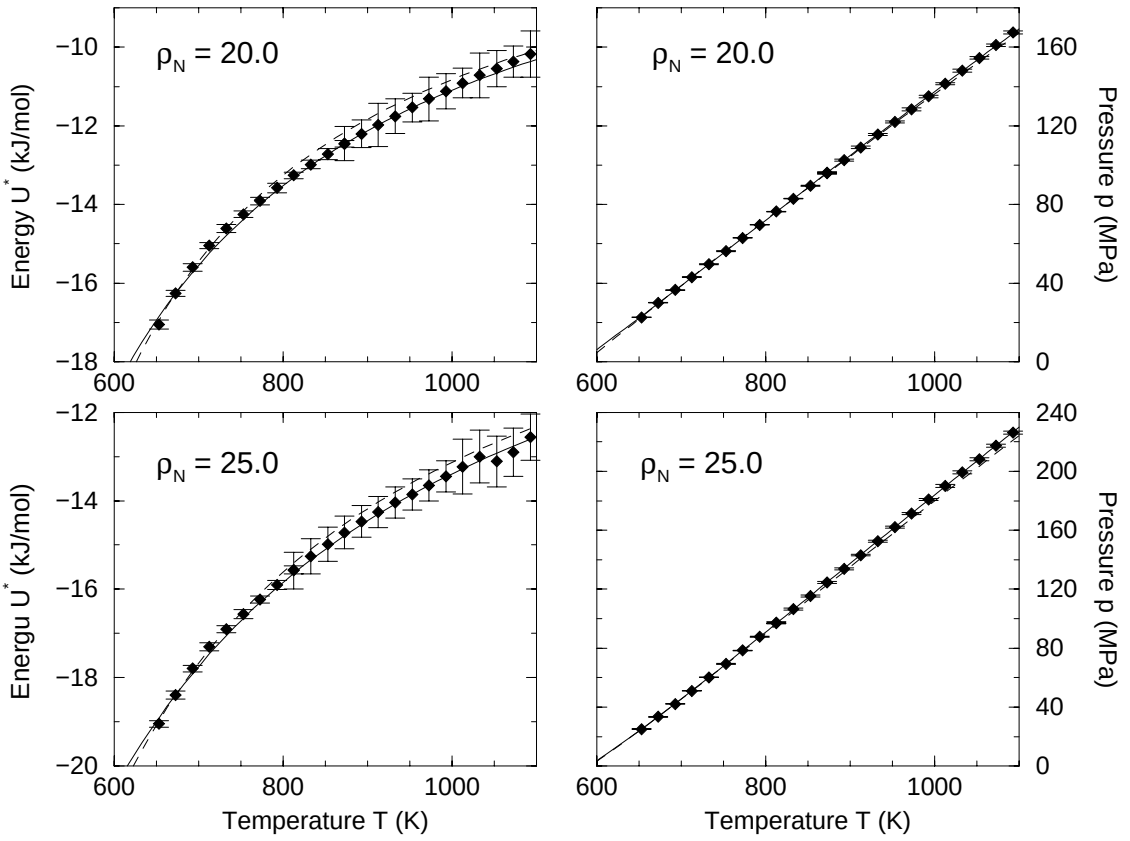

Figure 7.2: Experimental data of U^* and p for $\rho_N = 20$ and 25 mol/dm^3 (♦), and Gamma state predictions: parameter set **1** *(——) and set* **4** *(– – –).*

(RMSD), defined as

$$\text{RMSD } X = \sqrt{\frac{1}{N_{data}} \sum_{i}^{N_{data}} \left(X_i - X_{i,exp}\right)^2} \tag{7.28}$$

and the percent average absolute deviation, % AAD, defined as

$$\%\text{AAD } X = \frac{1}{N_{data}} \sum_{i}^{N_{data}} \left| \frac{X_i - X_{i,exp}}{X_{i,exp}} \right| \tag{7.29}$$

Results are given in Tables 7.2, 7.3 and 7.4. From these tables it is clear that both the energy U^* and especially the free energy A' are reproduced very well by all the confined Gamma states. The corresponding values of χ^2 and RMSD are excellent, and the results of sets **2**, **3** and **4** differ only very little, indicating

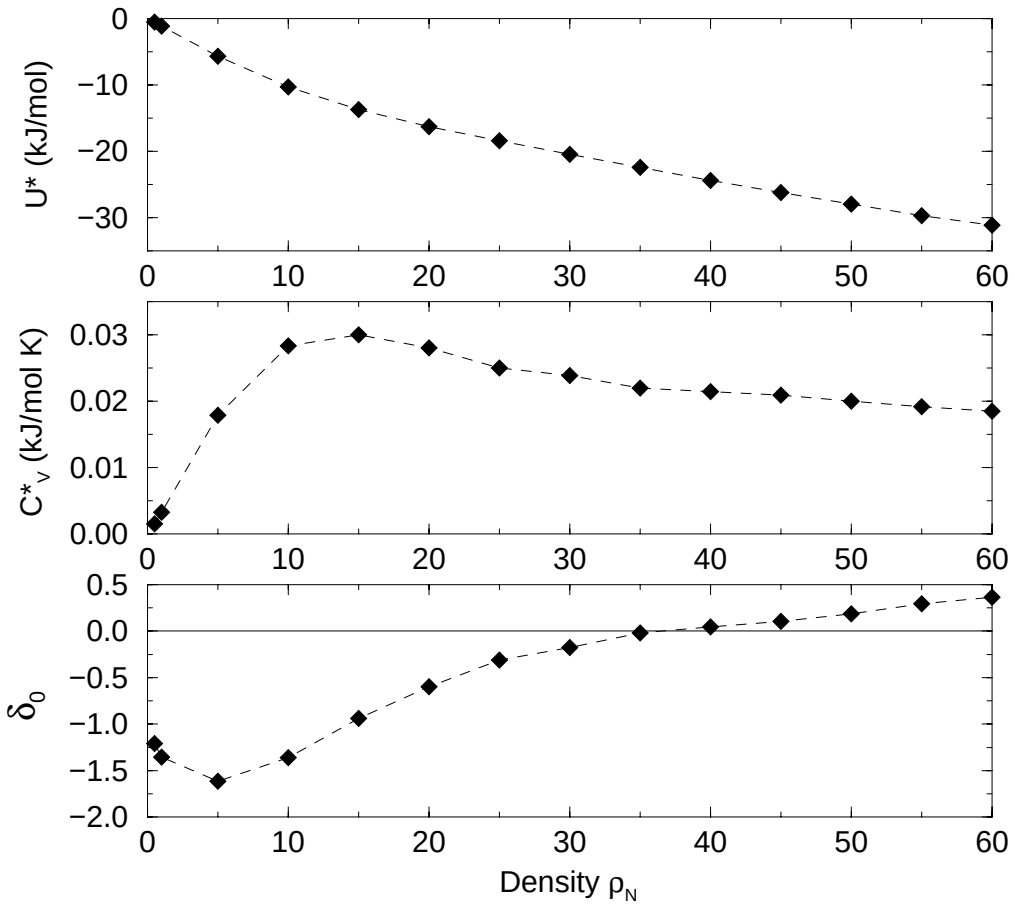

Figure 7.3: Behaviour of the parameters U_0^*, C_{V0}^* and δ_0 as a function of density at $T_0 = 673$ K, for parameter set **1**.

the stability of the procedure to obtain the parameters using only a minimum of local information. The agreement between experimental and predicted pressure is also good; the average relative error never exceeds 1.6%, while the RMSD is somewhat larger because of the large pressure interval (up to 1000 MPa).

Smits *et al.*[121] have parametrized a two and three-site APACT equation of state for water, based on experimental vapour pressure and liquid density PVT data up to the critical temperature, and report only % AAD values for the pressure. For the same temperature and pressure range as used in this article ($T \leqslant 1073$ K, $p \leqslant 1000$ MPa), we find from their Tables 2 and 3 for the three-site APACT the value % AAD = 1.90% (and 2.18% for $p \leqslant 100$ MPa) and % AAD = 2.32% (for $p \leqslant 100$ MPa) for the two-site version. This is clearly comparable, but slightly higher than our value of $\sim 1.6\%$ (Table 7.4), eventhough we only used very local data for the parameter sets **2**, **3** and **4**.

parameter set	N_{data}	χ^2/N_{df}	RMSD (kJ/mol)	% AAD (%)
1. A^* fit + p fit	354	0.01	0.025	0.47
2. $U^*(T_{0,loc}+20)$ + p' local	354	0.04	0.085	2.85
3. $U^*(T_{0,loc}+40)$ + p' local	354	0.04	0.082	3.02
4. $U^*(T_{0,loc}+60)$ + p' local	354	0.03	0.077	3.06

Table 7.2: Statistical analysis of the free energy (A') predictions using different methods to obtain the Gamma state parameters, where in this case $N_{df} = N_{data} - 43$.

parameter set	N_{data}	χ^2/N_{df}	RMSD (kJ/mol)	% AAD (%)
1. A^* fit + p fit	354	0.64	0.19	1.13
2. $U^*(T_{0,loc}+20)$ + p' local	354	2.18	0.32	2.05
3. $U^*(T_{0,loc}+40)$ + p' local	354	1.68	0.30	1.89
4. $U^*(T_{0,loc}+60)$ + p' local	354	1.25	0.29	1.79

Table 7.3: Statistical analysis of the energy (U^*) predictions using different methods to obtain the Gamma state parameters, where in this case $N_{df} = N_{data} - 43$.

parameter set	N_{data}	χ^2/N_{df}	RMSD (MPa)	% AAD (%)
1. A^* fit + p fit	354	12.7	3.3	1.54
2. $U^*(T_{0,loc}+20)$ + p' local	354	29.5	11.8	1.59
3. $U^*(T_{0,loc}+40)$ + p' local	354	28.6	11.8	1.58
4. $U^*(T_{0,loc}+60)$ + p' local	354	28.0	11.8	1.56

Table 7.4: Statistical analysis of the pressure (p) predictions using different methods to obtain the Gamma state parameters, where in this case $N_{df} = N_{data} - 42$.

7.6 Conclusions

In this article we systematically applied the confined Gamma state level of the quasi-Gaussian entropy theory to water isochores up to 1073 K and 60 mol/dm^3. The predictions of this statistical state agree very well with the experimental data, even in the critical point region, which was not investigated before.

We compared different methods to obtain the isochore parameters: besides the values of energy and entropy at the local reference temperature, which was chosen to be close to the coexistence line, we used (1) an overall non-linear fit on the excess free energy and the pressure, and (2) an evaluation using only one extra energy value at a slightly higher temperature than the local reference temperature, combined with a local pressure polynomial fit. Both methods gave very similar and stable results with comparable accuracy.

These results also show that it is possible to obtain reliable estimates of the isochore parameters of the confined Gamma state using a minimal amount of experimental data at moderate conditions, and hence the parametrization of equations of state, where only a limited set of experimental data may be available, is in principle possible using this theory.